



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> PAPER SIZING COMPOSITION		
<b>(57) Abstract</b>  The present invention relates to a composition for use in sizing paper, the paper sizing composition comprises an aqueous alkenyl succinic anhydride (ASA) emulsion wherein the particles of the emulsion have a coating of an insoluble salt of alkenyl succinic acid.		

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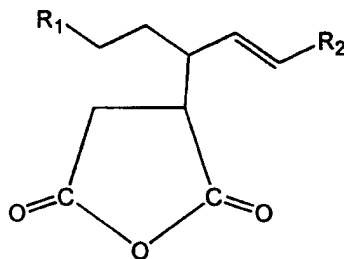
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### PAPER SIZING COMPOSITION

The present invention relates to a composition for use in sizing paper and more particularly to such a composition containing alkenyl succinic anhydride (ASA) as the active sizing agent.

Paper sizing may be effected using a number of different materials. For example, it is known to effect sizing using a rosin emulsion in conjunction with an aluminium salt (e.g. papermakers' alum) which is effective to cause deposition of the rosin and to the fibres being sized. It is also known to use reactive sizes, e.g. alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). The latter is more reactive than the former and consequently is preferred as a reactive sizer.

ASA is normally made by the reaction of a mixture of long chain (e.g.  $C_{16-18}$ ) olefins with maleic anhydride to produce a product generally represented by the formula: -



where  $R_1$  and  $R_2$  are the same or different alkyl chains. Since a mixture of olefins are used in the production of ASA, the resulting product is a liquid. The liquid is converted to an emulsion in water for use as a paper sizing composition.

ASA functions as a paper sizer by reacting with hydroxyl groups on cellulose fibres leading to the formation of succinate ester bonds. ASA is a preferred paper

sizer because of its high reactivity. This high reactivity has an associated disadvantage in that once the emulsion of ASA in water is prepared it is generally considered only to have a relatively short lifetime due to hydrolysis of the ASA to form alkenyl succinic acid. Typically, it is preferred that an ASA emulsion is used within an hour of being prepared and it tends to lose its effectiveness for paper sizing within 3-4 hours of preparation. Therefore ASA emulsions have to be prepared on-site at the paper mill since they have too short a life to be made at a suppliers production site and transferred by tanker to the mill. The reactivity of ASA thus leads to a number of disadvantages. Firstly, costly homogenisation machinery has to be provided at the paper mill, often in duplicate to ensure continuity of supply. Secondly, if the machinery for producing the ASA emulsion breaks down then the paper mill must suspend production. Thirdly, if the paper making machine has to stop for any reason then ASA emulsion in holding tanks can degrade and may ultimately need to be discarded.

Alkenyl succinic acid is also produced (by hydrolysis of ASA) during the paper making process and gives rise to a so-called "stickie" at the wet end of the paper making machine. "Stickies" are those adhesive organic substances that are to be found at various places in the wet end of a paper machine and give rise to particular problems on wires, felts and press rolls. The paper maker has long used the addition of paper makers alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 16-18 \text{ H}_2\text{O}$ ) to retain these compounds in the paper making sheet. The alum helps to prevent deposits of the alkenyl succinic acid, or some of its salts, forming on the paper making machine at the wet end by retaining the diacid in the wet web as aluminium alkenylsuccinate. Whilst the problem of "stickies" associated with the use of ASA emulsions has previously been addressed, little attention has been given (as far as we are aware) to the stability of ASA emulsions.

It is therefore an object of the present invention to obviate or mitigate the abovementioned disadvantages.

According to a first aspect of the present invention there is provided a paper sizing composition comprising an aqueous alkenyl succinic anhydride emulsion wherein the particles of the emulsion have a coating of an insoluble salt of alkenyl succinic acid.

Thus in accordance with the invention there is provided an ASA emulsion in which the "droplets" of the emulsion have a coating (which may be a partial or complete coating) of an insoluble salt of alkenyl succinic acid. We have found, and this forms the basis of the present invention, that the provision of such a coating considerably improves the stability of the emulsion and its resistance to hydrolysis. Whilst not wishing to be bound by theory, we believe that the coating of the insoluble salt acts as a barrier which slows down or reduces the transport of water molecules to the ASA droplets thus slowing its hydrolysis to alkenyl succinic acid.

The insoluble salt may for example, be of an inorganic cation such as aluminium, copper, iron ( $\text{Fe}^{3+}$ ) or calcium salt. It is particularly preferred that the salt is the aluminium salt. We have in fact found that the use of the aluminium salt may extend the life of an ASA emulsion tenfold, as compared to a similar emulsion, in which the film coating is not provided.

Typically the amount of the cation will generally be  $1 \times 10^{-6}$  to  $1 \times 10^{-2}$ , preferably  $1 \times 10^{-5}$  to  $5 \times 10^{-3}$ , moles per gramme of ASA. Even more preferably the amount of the cation is in the range  $5 \times 10^{-4}$  to  $1 \times 10^{-3}$  on the same basis.

The emulsion in accordance with the invention may be produced by emulsifying ASA in the presence of the cation which forms the insoluble salt with alkenyl succinic acid. This may be effected in a number of ways. For example, the cation may be dissolved in an aqueous medium and the ASA is then emulsified into

this medium. Alternatively, the cation may be admixed with the ASA which is then emulsified into water.

In all cases, emulsification may be effected using well known techniques for production of ASA emulsions.

For the purposes of producing the emulsion, the cation may be provided in the form of a simple, usually inorganic salt. The salt should be water soluble and may, for example, be a halide, sulphate, nitrate or oxide. The amount of the salt used during production of the emulsion will generally be up to 60% by weight of the ASA.

It is particularly preferred to use crystalline aluminium sulphate as the inorganic salt. Conveniently this may be provided as papermakers alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 16-18 \text{H}_2\text{O}$ ).

It is preferred that the ASA as used for forming the emulsion is a liquid at room temperature. Suitable ASAs may be produced by reaction of a mixture of  $\text{C}_{16-18}$  olefins with maleic anhydride. Such ASAs are commercially available.

It will generally also be appropriate to use a stabiliser in the formation of the emulsion. Examples of suitable stabilisers are well known in the art and include, for example, starch, ionic starch including cationic and anionic starch, (e.g. potato or waxy maize starch) or a cationic polyacrylamide or other cationic polymer. The amount of stabiliser used is usually up to 25% by weight based on the weight of ASA, more preferably 5% to 20% on the same basis.

Optionally the emulsion will contain at least one surfactant. Examples of suitable surfactants are well known in the art and include, for example, phosphate, esters, phosphate ethers, nonyl phenol ethoxylates, polyacrylamides, and

lignosulphonic acid derivatives. The amount of surfactant used is generally up to 5% by weight of ASA.

The emulsion in accordance with the invention may be used in an entirely conventional means for sizing of fibres to be used for the formation of paper, board and like material. For this purpose, the emulsion will be added to the wet-end of a paper making process and may be added to the so-called thick stock (usually comprised of 2% to 5%, e.g. about 3%, by weight of the papermaking fibres) or to the thin stock (usually comprised of up to 1%, e.g. about 0.5% by weight of the papermaking fibres). Alternatively the ASA emulsion may be added at the size press.

The invention will now be further described with reference to the following Examples.

#### **Example 1**

An emulsion in accordance with the invention was prepared by emulsifying an admixture of 10 g of a commercial ASA (P68F supplied by Pentagon) and  $5.0 \times 10^{-3}$  moles crystalline papermakers alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 16-18 \text{ H}_2\text{O}$ ) into sufficient of a 1% by weight solution of Hicat 168 (a starch supplied by Roquette) to produce 200 ml of emulsion. The emulsification procedure was effected using a Silverson laboratory mixer operating at full speed for 2 minutes.

The emulsion was monitored at half-hourly intervals at 40°C to determine the amount of ASA in the emulsion. Monitoring was by means of infra-red analysis using Attenuated Total Internal Reflectance Spectroscopy (ATR) (32 scans, resolution 4). A Spectra-Tech Thermal ARK (Attenuated Total Reflectance Kit) was employed to carry out the experiments. The ARK was equipped with a 45° ZnSe crystal. The emulsion was sampled directly onto the crystal with a water spectrum subtracted from the resulting spectrum, thereby eliminating water (-OH) absorption peaks from the emulsion spectrum. The areas of the alkenyl succinic anhydride (ASA)/alkenyl

succinic acid (ASAcid) peaks were then calculated in a method described by Takeda (Y.Takeda, Dept. of Paper Science, UMIST, PhD Thesis, 1993). In this and all other instances the peaks were measured between the following limits: 1882.214-1824.659  $\text{cm}^{-1}$ , 1824.659-1751.077  $\text{cm}^{-1}$  and 1751.077-1681.551  $\text{cm}^{-1}$ .

The results are shown in the "Alum" column of Table 1.

For the purposes of comparison a "standard" ASA emulsion was prepared by the method described above but without the addition of alum, and monitored at 40°C, at half hourly intervals for ASA content using the abovedescribed technique. The results of this experiment are shown in the "Standard" column of Table 1

It was observed that the pH of the emulsion containing  $5 \times 10^{-3}$  moles crystalline  $\text{Al}_2(\text{SO}_4)_3$  was lower than that of the "Standard" emulsion. In order to determine whether the hydrolysis rate was a function of emulsion pH, the pH of a "Standard" ASA emulsion was altered using a mineral acid. This solution was also monitored at 40°C, at half hourly intervals. The results of this experiment are shown in Table 1 in the "pH Adj." column.



**Table 1**

Time/Hours	%ASA Remaining		
	Alum	Standard	pH Adj.
0	100.00	99.43	100.00
1.0	100.00	95.02	97.50
1.5	100.00	93.45	100.00
2.0	100.00	86.85	94.04
2.5	100.00	89.26	95.69
3.0	100.00	79.51	93.50
3.5	100.00	82.78	87.26
4.0	100.00	81.47	85.21
4.5	100.00	83.19	84.07
5.0	99.98	76.15	76.65
5.5	99.87	72.11	75.10
6.0	99.41	67.07	67.65
6.5	95.46	61.90	52.22
7.0	99.46	55.56	39.62
7.5	96.27	46.37	21.91
8.0	91.51	38.86	2.42

The Table shows that the hydrolysis of ASA to ASAcid was significantly reduced by the use of  $5 \times 10^{-3}$  molar crystalline  $\text{Al}_2(\text{SO}_4)_3$  and also that this effect was not merely a result of the reduction of the pH of the solution caused by the solvation of the  $\text{Al}^{3+}$  salt.

### **Example 2**

ASA emulsions were prepared as in Example 1 containing  $5 \times 10^{-3}$  moles and  $1 \times 10^{-2}$  moles papermakers alum. The hydrolytic stability of the emulsions was monitored at room temperature at half hourly intervals using the ATR technique described in Example 1. The procedure was carried out in triplicate and the average of the results are shown in Table 2.

Table 2

Time/Hours	%ASA Remaining	
	$5 \times 10^{-3}$ M	$1 \times 10^{-2}$ M
16.0	99.67	100.00
16.5	99.94	100.00
17.0	99.75	100.00
17.5	99.06	100.00
18.0	99.82	100.00
18.5	97.85	100.00
19.0	95.36	100.00
19.5	90.97	99.20
20.0	89.73	99.01
20.5	87.29	98.53
21.0	86.27	98.16
21.5	86.08	97.27
22.0	84.11	97.35
22.5	80.23	97.14
23.0	82.13	98.09
23.5	78.03	95.92
24.0	82.92	95.55
24.5		91.88
25.0		86.10
25.5		86.72
26.0		86.26
26.5		84.09
27.0		88.44
27.5		79.97
28.0		77.33
28.5		75.99
29.0		67.79

This experiment shows that the higher concentration of crystalline  $\text{Al}_2(\text{SO}_4)_3$  in the ASA emulsion slows the hydrolysis of ASA to ASAcid even further and indeed prevents any hydrolysis occurring for 19 hours at room temperature.

**Example 3**

An ASA emulsion was prepared as in Example 1 using  $1 \times 10^{-2}$  moles papermakers alum. A comparison ("Standard") emulsion was prepared without the alum. The hydrolytic stability of the emulsions was monitored as in Example 1 at 30°C, at half hourly intervals. The procedure was carried out in triplicate and the average results are presented in Table 3.

**Table 3**

Time/Hours	%ASA Remaining	
	Standard	$1 \times 10^{-2}$ M
0	100.00	100.00
1.0	98.10	100.00
1.5	97.84	100.00
2.0	98.30	100.00
2.5	98.10	100.00
3.0	97.03	100.00
3.5	91.68	100.00
4.0	94.23	100.00
4.5	92.07	100.00
5.0	88.05	100.00
5.5	86.32	100.00
6.0	79.80	100.00
6.5	80.33	100.00
7.0	87.07	100.00
7.5	82.98	100.00
8.0	80.91	100.00
16.0	48.94	90.80
16.5	29.48	87.56
17.0	22.44	82.75
17.5	23.51	76.02
18.0	15.01	74.75
18.5	2.66	73.05
19.0	0.00	70.22
19.5		57.88
20.0		61.25
20.5		52.42
21.0		49.53
21.5		43.79
22.0		48.26
22.5		39.28
23.0		27.31
23.5		21.92
24.0		20.36

The results of this experiment in conjunction with the results of the experiments of Examples 1 and 2 show how the hydrolysis of ASA to ASAcid is

slowed greatly by the use of  $1 \times 10^{-2}$  moles of alum. After 19 hours when the standard solution is completely hydrolysed the solution containing  $\text{Al}_2(\text{SO}_4)_3$  still has over 70% of the original ASA remaining.

#### **Example 4**

Two emulsions in accordance with the invention were prepared as in Example 1 but using  $5 \times 10^{-3}$  moles  $\text{CuCl}_2$  and  $1 \times 10^{-2}$  moles  $\text{CuCl}_2$  instead of papermakers alum. A further emulsion in accordance with the invention was prepared as described in Example 1 using  $5 \times 10^{-3}$  moles papermakers alum. A comparison "Standard" emulsion was prepared which did not include either  $\text{CuCl}_2$  or papermakers alum. The hydrolytic stability of the emulsions was monitored after 21 hours at room temperature using the technique described in Example 1. The results are shown in Table 4.

**Table 4**

Emulsion	ASA Remaining %
Standard	49.59
$5 \times 10^{-3}$ M Alum	98.16
$1 \times 10^{-2}$ M $\text{CuCl}_2$	86.27
$5 \times 10^{-3}$ M $\text{CuCl}_2$	84.11

This experiment shows that although  $\text{CuCl}_2$  is effective at slowing the rate of hydrolysis of ASA to ASAcid it is not as effective as alum. More particularly, the emulsion prepared with  $5 \times 10^{-3}$  moles  $\text{CuCl}_2$  contained 84.11% of ASA after 21 hours as compared to 98.16% for the emulsion prepared with alum. A higher amount of  $\text{CuCl}_2$  ( $1 \times 10^{-2}$  moles) improves the situation slightly (86.27% ASA remaining).

**Example 5**

An emulsion in accordance with the invention was prepared as in Example 1 but using  $5 \times 10^{-3}$  moles and  $1 \times 10^{-2}$  moles crystalline  $\text{CuCl}_2$  instead of papermakers alum. A "Standard" emulsion which contains neither  $\text{CuCl}_2$  nor alum was also prepared. The hydrolytic stability of the two emulsions was monitored as in Example 1 at  $30^\circ\text{C}$  at half hourly intervals. The procedure was carried out triplicate and the average results are presented in Table 5.

**Table 5**

Time/Hours	%ASA Remaining		
	Standard	$5 \times 10^{-3} \text{ M CuCl}_2$	$1 \times 10^{-2} \text{ M CuCl}_2$
0	100.00	100.00	
1.0	98.10	100.00	100.00
1.5	97.84	100.00	100.00
2.0	98.30	100.00	100.00
2.5	98.10	100.00	100.00
3.0	97.03	100.00	100.00
3.5	91.68	100.00	100.00
4.0	94.23	97.30	100.00
4.5	92.07	99.10	100.00
5.0	88.05	100.00	99.04
5.5	86.32	97.68	100.00
6.0	79.80	95.51	98.75
6.5	80.33	95.42	99.43
7.0	87.07	95.76	99.04
7.5	82.98	91.86	99.58
8.0	80.91	91.58	99.01

This experiment shows that the rate of hydrolysis of ASA to ASAcid is significantly reduced by the addition of  $5 \times 10^{-3}$  moles  $\text{CuCl}_2$  to the ASA emulsion. This experiment also shows that the higher concentration of crystalline  $\text{CuCl}_2$  in the ASA emulsion slows the hydrolysis of ASA to ASAcid even further.

**Example 6**

An emulsion in accordance with the invention was prepared as in Example 1 but using  $5 \times 10^{-3}$  moles and  $1 \times 10^{-2}$  moles crystalline  $\text{CuCl}_2$  instead of papermakers alum. A "Standard" emulsion which contains neither  $\text{CuCl}_2$  nor alum was also prepared. The hydrolytic stability of the two emulsions was monitored as in Example 1 at  $40^\circ\text{C}$  at half hourly intervals. The procedure was carried out triplicate and the average results are presented in Table 6.

**Table 6**

Time/Hours	%ASA Remaining		
	Standard	$5 \times 10^{-3} \text{ M CuCl}_2$	$1 \times 10^{-2} \text{ M CuCl}_2$
0	99.43	100.00	100.00
1.0	95.02	100.00	100.00
1.5	93.45	100.00	100.00
2.0	86.85	100.00	100.00
2.5	89.26	100.00	100.00
3.0	79.51	100.00	100.00
3.5	82.78	100.00	100.00
4.0	81.47	98.12	100.00
4.5	83.19	95.96	100.00
5.0	76.15	93.07	100.00
5.5	72.11	96.75	99.34
6.0	67.07	88.71	97.86
6.5	61.90	90.01	94.42
7.0	55.56	84.31	89.85
7.5	46.37	79.42	88.58
8.0	38.86	72.65	76.36

This experiment shows that the rate of hydrolysis of ASA to ASAcid is significantly reduced by the addition of  $5 \times 10^{-3}$  moles  $\text{CuCl}_2$  to the ASA emulsion. This experiment also shows that the higher concentration of crystalline  $\text{CuCl}_2$  in the ASA emulsion slows the hydrolysis of ASA to ASAcid even further.

### Conclusions

Both  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{CuCl}_2$  have been shown to significantly reduce the rate of hydrolysis of ASA to ASAcid at ambient and at elevated temperatures. In each case the higher the concentration of the metal salt the larger the reduction in the rate of hydrolysis.

Of the two  $\text{Al}_2(\text{SO}_4)_3$  has been shown to be the most effective agent in prolonging the lifetime of an aqueous emulsion of ASA. This result has been shown to be unrelated to the lowering of the pH of the aqueous emulsion caused by the solvation of the aluminium salt.



### Claims

1. A paper sizing composition comprising an aqueous alkenyl succinic anhydride(ASA) emulsion wherein the particles of the emulsion have a coating of an insoluble salt of alkenyl succinic acid.
2. A composition according to claim 1, wherein the cation of the insoluble salt is an inorganic cation.
3. A composition as claimed in claim 2 wherein the cation is aluminium, copper, iron or calcium.
4. A composition as claimed in claim 3 wherein the cation is aluminium.
5. A composition as claimed in any one of claims 1 to 4 wherein the amount of the cation is in the range  $1 \times 10^{-6}$  to  $1 \times 10^{-2}$  moles per gramme of ASA.
6. A composition as claimed in claim 5 wherein the amount of the cation is in the range of  $1 \times 10^{-5}$  to  $5 \times 10^{-3}$  moles per gramme of ASA.
7. A composition as claimed in 6 wherein the amount of the cation is in the range  $5 \times 10^{-4}$  to  $1 \times 10^{-3}$  moles per gramme of ASA.
8. A composition as claimed in any one of claims 1 to 7 which includes at least one cationic stabiliser.
9. A composition as claimed in claim 8 wherein the cationic stabiliser is a starch or a polyacrylamide or other cationic polymer.

10. A composition according to claim 8 or 9 wherein the stabiliser is present in the emulsion in an amount up to 25% by weight if the ASA.
11. A composition according to any one of claims 1 to 10 wherein the composition includes at least one surfactant.
12. A composition as claimed in claim 11 wherein the surfactant is selected from phosphate esters, phosphate ethers, nonyl phenol ethoxylates, polyacrylamides, and lignosulphonic acid derivatives.
13. A method of producing a paper sizing composition comprising emulsifying ASA in water in the presence of a cation which forms an insoluble salt with alkenyl succinic acid.
14. A method as claimed in claim 13 wherein the emulsion is prepared by dissolving the cation in the water and then emulsifying the ASA into the solution of the cation.
15. A method as claimed in claim 13 wherein the emulsion is prepared by admixing the cation with the ASA and emulsifying the admixture of the ASA and the cation into water.
16. A method as claimed in any one of claims 13 to 15 for the production of an emulsion as claimed in any one of claims 1 to 12.
17. The use of a composition as claimed in any one of claims 1 to 12 as a sizing agent for the formation of paper, board or like materials.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/03113

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D21H17/16 D21H21/10 C07C57/13

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D21H C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2201171 A	24-08-1988	NONE	